

May 29, 1884.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Mr. Henry B. Medlicott (elected 1877) was admitted into the Society.

The following Papers were read:—

- I. "The Conditions of Chemical Change in Gases: Hydrogen, Carbonic Oxide, and Oxygen." By HAROLD B. DIXON, M.A. Communicated by Professor A. W. WILLIAMSON, Foreign Sec. R.S. Received May 15, 1884.

(Abstract.)

Bunsen,\* in 1852, exploded mixtures of carbonic oxide and electrolytic gas in different proportions in order to test the correctness of the "Law of Mass." According to this law the division of oxygen between two combustible gases depends both on the relative affinity of the two combustibles for oxygen, and on the quantities of them present. In 1857 Bunsen† published some further experiments on the same subject. He concluded from his results that the Law of Mass was modified in a particular way by the tendency of the atoms to form simple hydrates of carbonic acid; so that the ratio of carbonic oxide to hydrogen might be changed within certain limits without altering the proportion in which the oxygen divides itself; but, on still further changing the ratio of carbonic oxide to hydrogen, the proportion in which the oxygen divides itself changes *per saltum*. The ratio between the carbonic acid and the steam produced in the explosion might always be expressed, according to Bunsen, by small integers.

In 1874 E. v. Meyer‡ published experiments on the incomplete combustion of mixtures of carbonic oxide and hydrogen by oxygen

\* "Ann. Chem. Pharm.," lxxxv, 137.

† Bunsen, "Gas Meth.," 1857.

‡ "Journ. Prakt. Chem." (ii), x, 273.

and by nitrous oxide. He concluded that the division of the oxygen between the combustible gases changes *per saltum*, and that the ratio between the carbonic acid and steam produced might always be expressed by whole numbers, but not always by small integers.

v. Meyer found that the presence of an inert gas, nitrogen, favoured the formation of carbonic acid. He also found that more steam was generally formed when the explosions were made in narrow tubes than when they were made in wide tubes.

In 1876 Horstmann\* published a paper in a local journal at Heidelberg in which he showed that Bunsen's results were vitiated by his having exploded the gaseous mixtures in a eudiometer saturated with aqueous vapour. At the high temperature of the explosion, steam oxidises carbonic oxide, so that the proportion of carbonic acid found after the explosion partly depended upon the initial temperature of the eudiometer, and the quantity of steam consequently present.

Horstmann showed that there was no discontinuous alteration in the ratio of the carbonic acid to steam formed in the explosion either in presence of aqueous vapour or without.

In the same year, 1876, in ignorance of Horstmann's paper, I repeated Bunsen's experiments, and came to the same conclusion as Horstmann. I found that the aqueous vapour in the eudiometer reacted with the excess of carbonic oxide at the high temperature reached. I repeated the experiments, drying the eudiometer and the gases carefully before exploding. My results gave no evidence of any change *per saltum* in the division of the oxygen.

In testing the dried gases it was discovered that an electric spark does not ignite a dry mixture of carbonic oxide and oxygen.† A trace of aqueous vapour was found to render the mixture explosive, all other conditions being the same. A mixture of the gases imperfectly dried with freshly fused potash was found to be unaffected by a spark at pressures below 500 millims. At a pressure of 500 millims. the mixture was ignited by the spark and burnt *slowly*. When left in contact with anhydrous phosphoric acid, either over mercury or sealed up in tubes, a mixture of two volumes of carbonic oxide with one of oxygen may be subjected, under atmospheric pressure, to powerful sparks from a coil or Leyden jar without exploding or igniting. The addition of a trace of steam, of dry hydrogen, dry ether vapour, dry pentane vapour, dry sulphuretted hydrogen, or dry hydrochloric acid vapour, was found to render the mixture inflammable, all the other conditions being the same. Dr. Bötsch‡ has published a paper in which he denies the non-inflammability of dry

\* "Verh. des Heidelb. Naturf. Med. Vereins," N.S., i, 3.

† "British Assoc. Report," 1880.

‡ "Liebig. Annalen," 1882.

carbonic oxide and oxygen; he considers that the inflammability of the mixture depends only upon pressure, and that in my experiments the mixture was tested under a less pressure when dry than when wet. This explanation of Dr. Bötsch's does not account for the facts observed. Under a pressure of 760 millims. the dry gases do not unite, while the wet mixture is explosive. The addition of a small quantity of nitrogen, carbonic acid, cyanogen, nitrous oxide, or carbon bisulphide, does not render the dry mixture inflammable.

The part played by the steam in the ordinary explosion of carbonic oxide and oxygen is similar to that of the nitric oxide in the sulphuric acid chamber. By suffering a succession of alternate reductions and oxidations the steam converts the carbonic oxide into carbonic acid. With very little steam this conversion is comparatively slow, so that in a nearly dry mixture there is no explosion, but the disk of flame is seen to travel slowly down the tube. With increasing quantities of aqueous vapour the rapidity of inflammation increases. An attempt\* was made to measure this increase in the velocity of explosion by observing the pressures produced in the eudiometer when equal masses of carbonic oxide and oxygen were fired under nearly identical conditions of temperature, pressure, and cooling surface, but with different proportions of steam. These experiments showed that the velocity of explosion increased with increasing quantities of steam, but they gave no absolute value for the rates of explosion. To obtain absolute rates direct measurements were made, with a chronograph, of the time which elapsed between the passage of the spark through the mixture, and the breaking of a thin silver bridge at the other end of the explosion tube about 1 metre from the firing point. The explosion tube of 13 millims. diameter was soldered into a metal trough, so that each end projected a short distance from the end of the trough. The trough was filled with water at the desired temperature. To determine the rate of explosion of the nearly dry gases, the mixture was forced slowly into the explosion tube (1) through two sulphuric acid drying tubes, and (2) through two long tubes containing anhydrous phosphoric acid. By removing the phosphoric acid tubes the gases were tested in a less dry state. By making the gases bubble slowly through a wash-bottle containing water at different temperatures below the temperature of the explosion tube, the quantity of steam added to the mixture could be approximately measured.

The following table gives the results of these velocity experiments:—

\* "British Assoc. Report," 1882.

Mean Rate of Explosion for the First Metre of Carbonic Oxide and Oxygen with different Quantities of Aqueous Vapour under Atmospheric Pressure.

Exploded at 10° C.		Exploded at 35° C.		Exploded at 60° C.	
Hygrometric state.	Rate in metres per sec.	Hygrometric state.	Rate in metres per sec.	Hygrometric state.	Rate in metres per sec.
Dried by passing slowly over fresh $P_2O_5$ .	36	Dried by passing slowly over fresh $P_2O_5$ .	44	Dried by passing slowly over fresh $P_2O_5$ .	53
		Dried by passing over $P_2O_5$ used above.	69		
Dried by bubbling through two bottles $H_2SO_4$ .	119	Dried by bubbling through 2 bottles $H_2SO_4$ . Ditto	102 103	Dried by bubbling through 2 bottles $H_2SO_4$ .	120
		Saturated at 6°. Ditto.	129 123		
		Saturated at 8°	155	Saturated at 8° Ditto	158 166
Saturated at 10°	175 176				
		Saturated at 12°	200	Saturated at 12°	211
		Saturated at 25° Ditto	225 226		
				Saturated at 35°	244
				Saturated at 50°	289
				Saturated at 60°	317

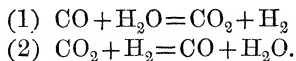
The velocity of explosion was found to increase rapidly from the point of inflammation. When a mixture of carbonic oxide and oxygen saturated with steam at 10° was exploded in a tube 13 millims. diameter, the velocity was found to be constant after the explosion had travelled 700 millims. along the tube. The constant velocity of the explosive wave attained under these conditions is rather over 1,500 metres per second. Berthelot and Vieille\* give

\* "Compt. Rend.," xcv, 151.

1,090 for the velocity of explosion of "dry" carbonic oxide and oxygen.

A comparison of the results obtained when dry carbonic oxide and electrolytic gas were exploded in a dried eudiometer with those obtained by Horstmann, and with those obtained by Bunsen,\* using a chain of sparks to fire the mixture, revealed the fact that both changes in the shape of the vessel and changes in the initial pressure under which the gases are fired, affect the division of the oxygen. By continually increasing the initial pressure, a pressure is reached where no further increase affects the division of the oxygen. At and above this "critical pressure," the division of the oxygen is also independent of the shape of the vessel. The larger the quantity of oxygen used the lower the critical pressure is found to be.

When dry mixtures of carbonic oxide and hydrogen in varying proportions are exploded above the "critical pressure" with oxygen insufficient for complete combustion, an equilibrium is established between two opposite chemical changes represented by the equations—



So that at the end of the reaction the product of the carbonic oxide and steam molecules is equal to the product of the carbonic acid and hydrogen molecules multiplied by a "coefficient of affinity." This result agrees with Horstmann's conclusion. But Horstmann considers the coefficient to vary with the relative mass of oxygen taken.

A small difference in the initial temperature at which the gases are fired makes a considerable difference in the products of the reaction. This difference is due to the condensation of steam on the sides of the vessel during the explosion, and its consequent removal from the sphere of action during the chemical change. When the gases are exploded at a temperature sufficiently high to prevent any condensation of steam during the progress of the reaction, the "coefficient of affinity" is found to be constant whatever the quantity of oxygen used, provided that the hydrogen is more than double the oxygen.

The presence of an inert gas, such as nitrogen, by diminishing the intensity of the reaction, favours the formation of carbonic acid in preference to steam. When the hydrogen is less than double the oxygen the excess of oxygen cannot react with any of the three other gases present—carbonic oxide, carbonic acid, and steam—but has to wait until an equal volume of steam is reduced to hydrogen by the

\* "Gasom. Meth.," 2te Auflage.

carbonic oxide. The excess of inert oxygen has the same effect as the inert nitrogen in favouring the formation of carbonic acid.

The variations in the coefficient of affinity found by Horstmann with different quantities of oxygen are due partly to this cause, but chiefly to the varying amounts of steam condensed by the cold eudiometer during the reaction in different experiments.

As the general result of these experiments it has been shown that when a mixture of carbonic oxide and hydrogen is exploded with insufficient oxygen for complete combustion, at a temperature at which no condensation of steam can take place during the reaction, and at a pressure greater than the critical pressure, an equilibrium between two opposite changes is established, which is independent of the quantity of oxygen taken, so long as this quantity is less than half the hydrogen. Within the limits marked out above, the law of mass is completely verified for the gaseous system composed of carbonic oxide, carbonic acid, hydrogen, and steam at a high temperature.

II. "On the Comparative Morphology of the Leaf in the Vascular Cryptogams and Gymnosperms." By F. O. BOWER, M.A., F.L.S. Communicated by W. T. THISELTON DYER, M.A., F.L.S. Received May 13, 1884.

(Abstract.)

Eichler, in his dissertation on the development of the leaf, defined the primordial leaf as the young leaf before internal differentiation or external distinction of parts; and further pointed out that subsequently two parts of it may be distinguished—the foliar base (*blattgrund*) which gives rise to the sheath and the stipules, if present, and the upper leaf (*oberblatt*) which develops into the simple branched lamina. The petiole is also, according to Eichler, derived from the upper leaf, though Goebel describes it as being intercalated between the two parts. The first part of the present paper is devoted to a discussion of this mode of treatment of the leaf. In accordance with the views clearly expressed by Sachs and others, the terms stem and leaf are to be regarded only as expressions denoting certain relationships of the parts of the *shoot*; the leaf is essentially an outgrowth from the stem. If this proposition be accepted, the same mode of morphological treatment ought to be applied to both. Now, in the treatment of the shoot as a whole, priority of importance is always attached to the mode of origin, and sequence of appearance of the several parts, while subsequent changes of conformation and dis-